

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
22 May 2003 (22.05.2003)

PCT

(10) International Publication Number
WO 03/043066 A2

(51) International Patent Classification⁷: **H01L 21/20**

Alan [GB/GB]; 40 Cavendish Mead, Sunninghill, Ascot, Berkshire SL5 9TD (GB).

(21) International Application Number: **PCT/IB02/04723**

(74) Agents: **CLELLAND, Sandra, Luischen et al.**; Spoor and Fisher, P.O. Box 41312, 2024 Craighall (ZA).

(22) International Filing Date:
12 November 2002 (12.11.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0127263.2 13 November 2001 (13.11.2001) GB

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(71) Applicant (*for all designated States except US*): **ELEMENT SIX LIMITED** [GB/GB]; Isle of Man Freeport, Ballasalla, Isle of Man IM99 6AQ (GB).

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (*for MW only*): **GILSON, David, Grant** [ZA/ZA]; Spoor and Fisher, Block A Rochester Place, 173 Rivonia Road, 2057 Morningside (ZA).

Published:

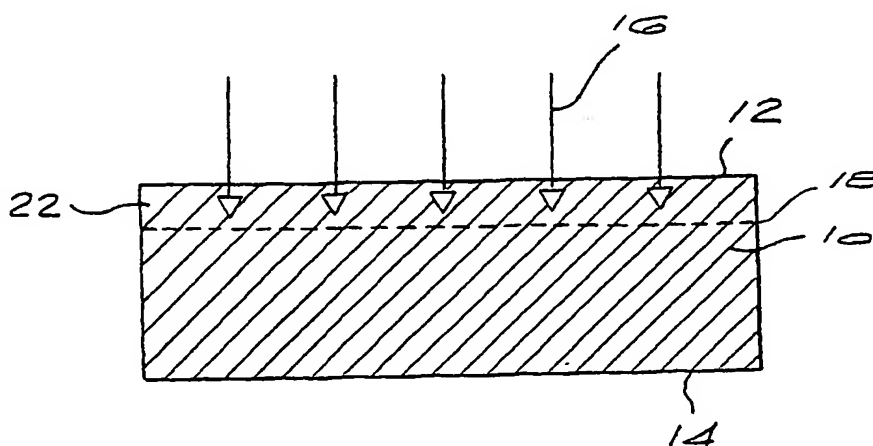
— without international search report and to be republished upon receipt of that report

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **WHITEHEAD, Andrew, John** [GB/GB]; 60 Cheylesmore Drive, Frimley, Camberley, Surrey GU16 9BW (GB). **TWITCHEN, Daniel, James** [GB/GB]; 10 Park Drive, Sunningdale, Berkshire SL5 0BD (GB). **SCARSBROOK, Geoffrey,**

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **LAYERED STRUCTURES**



(57) Abstract: A process of making a product which comprises at least two layers in contact with each other, each layer being of a wide-gap material and each layer differing from each other in at least one property, includes the steps of: (i) providing a substrate of a wide-band gap material having a surface and a region adjacent the surface having a particular characteristic, (ii) ion implanting the substrate through the surface to form a damaged layer below that surface, (iii) growing a layer of a wide-band gap material by chemical vapour deposition on at least a portion of the surface of the

substrate through which ion implantation occurred, the material of the grown layer having a characteristic different to that of the region of the substrate adjacent the surface through which ion implantation occurred, and (iv) severing the substrate through the damaged layer. The wide-gap material is preferably diamond.

WO 03/043066 A2

- 1 -

LAYERED STRUCTURES

BACKGROUND OF THE INVENTION

This invention relates to layered structures, particularly layered diamond structures.

For certain diamond applications, it is necessary to have two or more layers of diamond which have different properties in atomic contact with each other. One example is in electronics where a layered structures can be used to make a device, for example as described in WO 01/18882 A1

One method of making a layered diamond structure is by using ion implantation. Ions may be implanted into diamond to create an n-type or p-type semi-conducting layer on top of a layer with a different property. This method has the disadvantage that damage to the diamond occurs during ion implantation which can result in permanent degradation in important properties such as carrier lifetimes and mobilities. Further, the types and concentration of ions which can be successfully implanted in diamond are limited and the process often requires complex post implantation annealing.

CONFIRMATION COPY

- 2 -

Although chemical vapour deposition (CVD) provides a method of synthesising epi-layers, i.e. an epitaxially grown layer, to a desired thickness, the CVD process enables only a few very specific defects and impurities to be incorporated into the layer. This is best illustrated with the following example. A boron doped diamond layer can be grown onto a high purity single crystal substrate using a CVD process known in the art. The substrate might be processed from a natural diamond or diamond synthesised by CVD or high pressure high temperature (HPHT) methods. This will produce a two layer structure. Using conventional terminology this diamond structure will have *pi*-properties (i.e. properties exhibited by a sharp p-type to intrinsic semiconductor interface). Many of the typical two layer device structures that might be produced in this way require one of the layers to be very thin (<20 μm). For instance a 10 μm thick boron doped diamond layer on a 500 μm thick high purity diamond layer. A structure of this form, where precise thicknesses and sharp interfaces are necessary, requires considerable control of the synthesis process and/or careful mechanical processing of the structure following growth.

A CVD process is conducive to the synthesis of thin epi layers but has the disadvantage that only layers containing certain dopants can be synthesised. For example it is well known that HPHT synthesis provides a method of incorporating nickel, cobalt and nitrogen into the diamond in high concentrations (>5 parts per million (ppm) carbon atoms) but to date this has not been possible using CVD methods. Thus, to produce a diamond structure that consists of a thin epi-layer (<20 μm) containing nickel and a thicker boron doped layer (>100 μm) it would be necessary to take a suitably prepared substrate containing Ni with a thickness typically >200 μm (for ease of handling and processing) and then synthesise, using a CVD method, an overlayer (>100 μm) which contains the required boron concentration. Following growth, considerable care would then be needed with mechanical processing to finish with a structure which consists of, for example, a 10 μm Ni doped layer and a

- 3 -

100 μm B doped layer where the thickness tolerances are better than about 2 μm .

US Patent 5,587,210 describes a method of separating a CVD diamond layer from a diamond substrate. The method includes the steps of ion implanting a diamond substrate, thus creating a damaged layer of non-diamond carbon below the surface of the substrate through which ion implantation occurred, growing diamond on the surface of the substrate through which the ion implantation occurred, and electrochemically etching the diamond substrate to remove the damaged layer. The resulting product is a free standing CVD layer having a thin, i.e less than 1000 nm, layer of diamond bonded to a surface thereof.

The CVD diamond layer which is grown on the diamond substrate is pure CVD diamond. There is no suggestion that the CVD diamond layer should be doped or otherwise treated to change its electronic or other properties.

This US patent also suggests that the diamond substrate can be doped by ion implantation with suitable atoms to create n-type and p-type semi-conductors. When ion implanting a diamond substrate to create such semi-conductor properties, the implanted region will vary considerably in its dopant content. The region of highest and most uniform dopant concentration will lie below the surface through which ion implantation occurred. The region adjacent the surface through which the ion implantation occurred will contain little or no dopant and of non-uniform concentration. Thus, on either side of the interface between the substrate and the CVD diamond layer the material will be essentially pure diamond.

Furthermore, ion implantation doping is always associated with lattice damage due to the ion implantation, which substantially reduces the benefit obtained

- 4 -

from the dopant in that it adversely modifies the electronic properties of the doped layer.

SUMMARY OF THE INVENTION

According to the present invention, there is provided a process of making a product which comprises at least two layers in contact with each other, each layer being of a wide-band gap material and each layer differing from the other layer in at least one property, including the steps of:

- (i) providing a substrate of a wide-band gap material having a surface and a region adjacent the surface having a particular characteristic,
- (ii) ion implanting the substrate through the surface to form a damaged layer below that surface,
- (iii) growing a layer of a wide-band gap material by chemical vapour deposition on at least a portion of the surface of the substrate through which ion implantation occurred, the material of the grown layer having a characteristic different to that of the region of the substrate adjacent the surface through which ion implantation occurred, and
- (iv) severing the substrate through the damaged layer.

The ion implantation should be carried out with ions which allow deep penetration into the substrate, creating the damaged layer substantially below the surface through which the ion implantation occurs. The ions suitable to achieve this are typically ions of low atomic mass, preferably an atomic mass less than 21 and more preferably an atomic mass less than 13. Examples of suitable ions are helium and hydrogen ions. The ions for the ion implantation are preferably of high energy, e.g. have an energy exceeding 5 keV. The

- 5 -

precise depth of the damaged layer can be accurately controlled by manipulating the energy and type (i.e. mass) of the implanted ions. Typically, the ion implantation dose will exceed $1 \times 10^{15} \text{cm}^{-2}$.

Generally, the damaged layer will lie at a depth of 0,05 to 200 μm , typically 0,3 to 10 μm , below the surface through which ion implantation occurred.

It is preferred that the region of the substrate between the surface through which ion implantation occurs and the damaged layer is substantially free of ion implantation doping damage.

The wide-band gap material may be silicon carbide, gallium nitride or the like and is preferably diamond.

Generally, the layers will differ from each other in the characteristic which provides the layers with different electrical properties. The product may comprise only two layers in contact with each other, or more than two layers. When the product consists of more than two layers, adjacent layers, in contact with each other, will have different characteristics. The interface between adjacent layers defines a sharp and well-defined interface between two regions having different properties. This is an important feature, particularly when the layered product is to be used in an electronic application.

The surface through which the ion implantation occurs may be planar or non-planar. Thus, the interface between adjacent layers may also be planar or non-planar. When non-planar, the profile may be designed to provide a specific useful feature for a device which includes the layered product as a component.

*but not checked
the report was*

- 6 -

The substrate may be natural or synthetic diamond, particularly CVD diamond. The layer of grown wide-gap material may be CVD diamond or doped CVD diamond.

In one particular form of the invention, the region of the substrate adjacent to the surface through which ion implantation occurred is uniformly doped. The dopant may be selected from nitrogen, boron, nickel, cobalt, iron, phosphorus, sulphur or other elements which can occupy a lattice position, substitutional or otherwise, and provide the region with useful properties, particularly electronic properties.

The substrate and layer of grown wide-gap material may have the same thickness or differ in thickness. Generally, the layers will differ in thickness.

The process of the invention minimises excessive complicated post growth processing and enables structures that contain thin layers of diamond with properties very different to a second thicker layer to be synthesised. These structures have, for example, use in electronic applications.

DESCRIPTION OF THE DRAWING

The drawing illustrates, as Figures 1(a) to 1(c), schematically the steps in an embodiment of the invention.

DESCRIPTION OF EMBODIMENTS

The invention will now be illustrated with reference to the accompanying drawing. Referring to Figure 1a, a diamond substrate 10 has an upper surface 12 and a lower surface 14. High energy ions are implanted in the diamond

- 7 -

substrate 10 through surface 12, as illustrated by the arrows 16. The ions will typically be of light atoms such as hydrogen ions. The energy of the hydrogen ions will typically be between 20 keV and 5 MeV. The dose will typically be between $1 \times 10^{15} \text{cm}^{-2}$ and $1 \times 10^{20} \text{cm}^{-2}$. The ions penetrate to a depth indicated by dotted line 18. The diamond region 22 between the layer 18 and the surface 12 is not significantly damaged because the collision cross-section of the implanted ions is low at higher energies but rapidly increases as they slow down. Thus the surface layer through which the ions are implanted suffers relatively little damage, with the majority of the damage being confined to the narrow damage layer (region 18) required for subsequent release. The depth of region 18 below surface 12 may be in the range 0.05 μm to 200 μm , and more typically in the range 0.3 – 10 μm .

The diamond substrate 10 may be natural, or synthesised by chemical vapour deposition (CVD) or by high pressure high temperature (HPHT) techniques. This diamond will have characteristic electronic properties associated with some specific incorporated defect. Selection of this diamond substrate from any source of diamond provides for the broadest possible range of dopants, impurities or defects within the diamond with which to tailor its properties. The diamond substrate surface may be flat, for example a polished surface, or it may be curved or have non-planar features such as trenches or raised features which may subsequently form elements of, for example, an electronic device structure. This latter possibility arises because the nature of ion implantation is to allow penetration of the ions down to a given depth, independent of the macroscopic variation in height of the substrate. This provides for device geometries that are not easily achieved in diamond by any other means. In one example of the invention, the dopant in the substrate may be present from growth of the diamond, e.g. nickel, cobalt or iron. As the dopant is present from growth of the substrate, the substrate diamond is free of the ion damage that would be associated with ion implantation doping, and the

- 8 -

uniformity of the dopant is that of the original synthesis technique not the very non-uniform doping profile associated with ion implantation.

An epitaxial diamond layer 20 of different properties is then grown by CVD on the surface 12 of the substrate 10 (Figure 1b). The conditions necessary to produce CVD diamond growth are well known in the art. The thickness of the layer 20 will typically be greater than the region 22 defined between the surface 12 and the damaged layer 18. This region will have a particular characteristic differing from that of the grown layer 20. When the characteristic is imparted to the region by a dopant, that dopant will be uniformly distributed through the region. The surface 12 thus provides a very sharp boundary between the properties of the overgrown layer 20 and that of the region 22.

The diamond substrate is then severed along region 18, by immersing the product into an acid etch, annealing or using appropriate electrochemical etching. The resulting product (Figure 1c) is a layered product, in which diamond layer 20 has characteristics different to that of diamond layer 22. Interface 24 provides a sharp boundary between the characteristics of the two layers.

Implantation damage in the released layer 22 is generally low, since ion damage is low until the ion energy is almost exhausted which occurs as it reaches the damage layer 18. However, when using a substrate with a planar (preferably polished) surface, it is possible to reduce further the effect of this ion damage by implanting to a greater depth than is required (say to 5 μm), and after release removing a portion of the thickness of the released layer 22 by polishing, to leave a thinner final layer 22 (say 3 μm). This may be advantageous because the portion of diamond remaining had only higher energy ions traversing it, with proportionately lower ion damage, and the relatively heavily damaged region adjacent to the damaged region 18 is then wholly removed.

- 9 -

The process can be repeated more than once. For example bi-layer comprising the thin top layer 22 on a thicker layer 20 formed according to the invention can be further implanted through surface 26 of layer 22 into layer 20 to provide a damaged layer in layer 20. A thick CVD diamond layer is grown on surface 26 of layer 22 and then the sample severed along the implantation damaged layer. The result is a three layer structure, comprising the thin layer 22 sandwiched between a thin portion of the layer 20 and the new CVD diamond layer.

Example 1

A high purity diamond substrate produced using a CVD method known in the art with thickness 600 μm , is first implanted with 2 MeV oxygen ions to a dose of $1 \times 10^{17} \text{ cm}^{-2}$. A thick (300 μm) boron doped single crystal CVD layer which has, as measured by SIMS, $2 \times 10^{19} \text{ B atoms/cm}^3$ is grown on a surface of this substrate. Following growth the layered product is electrochemically etched to produce two samples: (i) a high purity diamond layer that can be reused and (ii) a two layer product consisting of a 1 μm high purity diamond layer and a 300 μm boron doped diamond layer in contact with the high purity diamond layer. This two layer product has an electronic application.

Example 2

A boron doped ($1 \times 10^{19} \text{ cm}^{-3}$) diamond substrate prepared using a CVD method with thickness 620 μm is first implanted with 2 MeV hydrogen ions to a dose of $1 \times 10^{19} \text{ cm}^{-2}$. A thick (300 μm) high purity single crystal CVD diamond layer is grown on to a surface of this substrate. Following growth the layered product is electrochemically etched to produce two samples: (i) a boron doped diamond plate which can be reused, and (ii) a two layer product consisting of

- 10 -

a 10 μm boron doped diamond layer and a 300 μm high purity diamond layer.
This two layer product has an electronic application.

CLAIMS

1. A process of making a product which comprises at least two layers in contact with each other, each layer being of a wide-band gap material and each layer differing from the other layer in at least one property, including the steps of:
 - (i) providing a substrate of a wide-band gap material having a surface and a region adjacent the surface having a particular characteristic,
 - (ii) ion implanting the substrate through the surface to form a damaged layer below that surface,
 - (iii) growing a layer of a wide-band gap material by chemical vapour deposition on at least a portion of the surface of the substrate through which ion implantation occurred, the material of the grown layer having a characteristic different to that of the region of the substrate adjacent the surface through which ion implantation occurred, and
 - (iv) severing the substrate through the damaged layer.
2. A process according to claim 1 wherein the ions used in the ion implantation are ions of low atomic mass.
3. A process according to claim 1 wherein the ions used in the ion implantation have an atomic mass of less than 21.
4. A process according to claim 1 wherein the ions used in the ion implantation have an atomic mass of less than 13.

- 12 -

5. A process according to claim 1 wherein the ions are helium or hydrogen ions.
6. A process according to any one of the preceding claims wherein ions of high energy are used in the ion implantation.
7. A process according to any one of the preceding claims wherein the ions used in the ion implantation have an energy exceeding 5 keV.
8. A process according to any one of the preceding claims wherein the ion implantation dose exceeds $1 \times 10^{15} \text{cm}^{-2}$.
9. A process according to any one of the preceding claims wherein severing of the substrate through the damaged layer is achieved by acid etching, annealing or electrochemical etching
10. A process according to any one of the preceding claims wherein the damaged layer lies at a depth of 0.05 to 200 μm below the surface through which ion implantation occurred.
11. A process according to any one of the preceding claims wherein the damaged layer lies at a depth of 0.3 to 10 μm below the surface through which ion implantation occurred.
12. A process according to any one of the preceding claims wherein the grown layer covers the entire surface of the substrate through which the ion implantation occurred.
13. A process according to any one of the preceding claims wherein the layers differ from each other in a characteristic which provides the layers with different electrical properties.

- 13 -

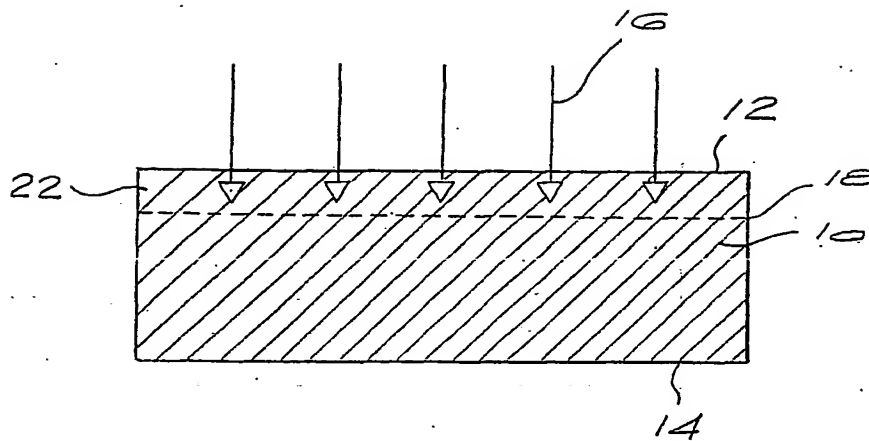
14. A process according to any one of the preceding claims wherein the wide band gap material is diamond.
15. A process according to any one of the preceding claims wherein the substrate is natural or synthetic diamond.
16. A process according to any one of the preceding claims wherein the substrate is CVD diamond.
17. A process according to any one of the preceding claims wherein the layer of grown wide-gap material is boron-doped diamond.
18. A process according to any one of the preceding claims wherein the region of the substrate adjacent the surface through which ion implantation occurred is uniformly doped.
19. A process according to claim 18 wherein the dopant is selected from nitrogen, boron, nickel, cobalt, iron, phosphorus and sulphur.
20. A process according to any one of the preceding claims wherein the substrate and layer of grown wide-gap material differ in thickness.
21. A process according to any one of the preceding claims wherein the surface through which ion implantation occurs is planar.
22. A process according to any one of the preceding claims wherein the surface through which ion implantation occurs is non-planar.
23. A process according to claim 1 substantially as herein described with reference to the accompanying drawing.

- 14 -

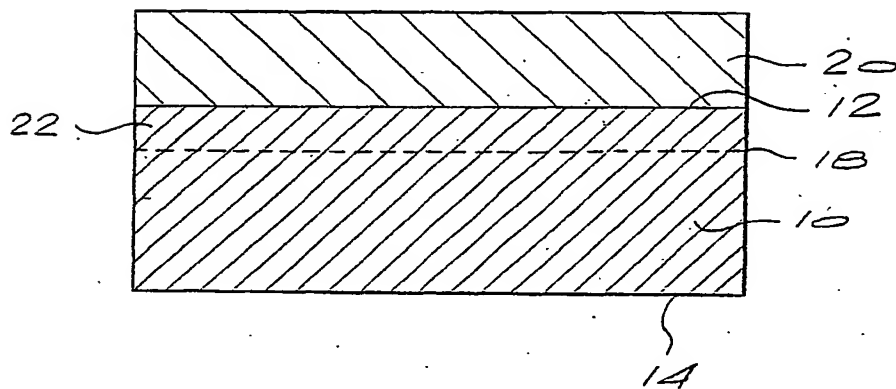
24. A process according to claim 1 substantially as herein described in either Example.

1
1

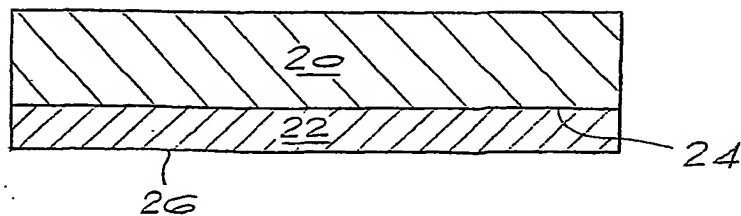
1(a)



1(b)



1(c)



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
22 May 2003 (22.05.2003)

PCT

(10) International Publication Number
WO 03/043066 A3

(51) International Patent Classification⁷: **H01L 21/20**,
C23C 16/27, 16/01, H01L 21/78

(21) International Application Number: PCT/IB02/04723

(22) International Filing Date:
12 November 2002 (12.11.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0127263.2 13 November 2001 (13.11.2001) GB

(71) Applicant (for all designated States except US): **ELEMENT SIX LIMITED** [GB/GB]; Isle of Man Freeport, Ballasalla, Isle of Man IM99 6AQ (GB).

(71) Applicant (for MW only): **GILSON, David, Grant** [ZA/ZA]; Spoor and Fisher, Block A Rochester Place, 173 Rivonia Road, 2057 Morningside (ZA).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **WHITEHEAD, Andrew, John** [GB/GB]; 60 Cheylesmore Drive, Frimley, Camberley, Surrey GU16 9BW (GB). **TWITCHEN,**

Daniel, James [GB/GB]; 10 Park Drive, Sunningdale, Berkshire SL5 0BD (GB). **SCARBROOK, Geoffrey, Alan** [GB/GB]; 40 Cavendish Mead, Sunninghill, Ascot, Berkshire SL5 9TD (GB).

(74) Agents: **CLELLAND, Sandra, Luischen et al.**; Spoor and Fisher, P.O. Box 41312, 2024 Craighall (ZA).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

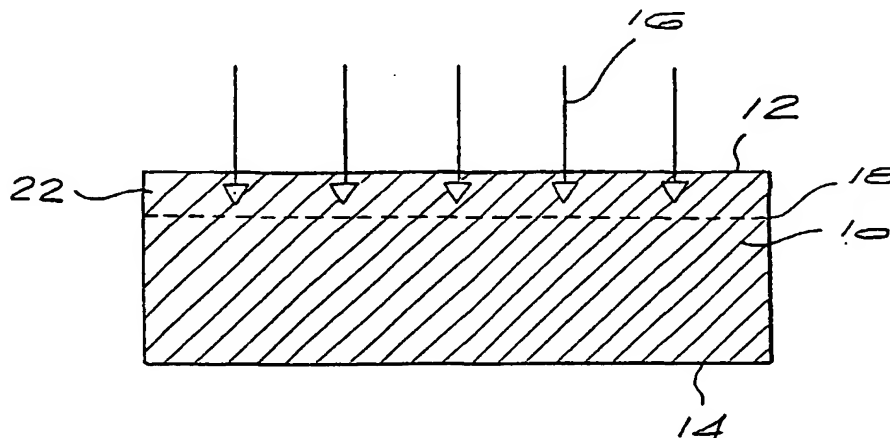
(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

[Continued on next page]

(54) Title: LAYERED STRUCTURES



(57) Abstract: A process of making a product which comprises at least two layers in contact with each other, each layer being of a wide-gap material and each layer differing from each other in at least one property, includes the steps of: (i) providing a substrate of a wide-band gap material having a surface and a region adjacent the surface having a particular characteristic, (ii) ion implanting the substrate through the surface to form a damaged layer below that surface, (iii) growing a layer of a wide-band gap material by chemical vapour deposition on at least a portion of the surface of the substrate through which ion implantation occurred, the material of the grown layer having a characteristic different to that of the region of the substrate adjacent the surface through which ion implantation occurred, and (iv) severing the substrate through the damaged layer. The wide-gap material is preferably diamond.

WO 03/043066 A3



(88) Date of publication of the international search report:
23 October 2003

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

INTERNATIONAL SEARCH REPORT

Intern Application No

PCT/TB 02/04723

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 H01L21/20 C23C16/27 C23C16/01 H01L21/78

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 H01L C23C C30B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-------------------------|
| X | US 5 587 210 A (MARCHYWKA MICHAEL J ET AL) 24 December 1996 (1996-12-24) cited in the application | 1-15, 20, 21, 23, 24 |
| Y | the whole document | 1-24 |
| Y | EP 0 479 625 A (DE BEERS IND DIAMOND) 8 April 1992 (1992-04-08) column 1, line 40 - line 46 | 1-15, 20, 21, 23, 24 |
| Y | EP 0 282 054 A (SUMITOMO ELECTRIC INDUSTRIES) 14 September 1988 (1988-09-14) abstract; example 2 | 16-19 |
| | --- -/- | |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

21 July 2003

Date of mailing of the international search report

30/07/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Le Meur, M-A

INTERNATIONAL SEARCH REPORT

Intern: .pplication No

PCT/IB 02/04723

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| Y | HIGUCHI K ET AL: "SELECTED AREA DIAMOND DEPOSITION BY CONTROL OF THE NUCLEATION SITES" DIAMOND AND RELATED MATERIALS, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 1, no. 2 - 4, 25 March 1992 (1992-03-25), pages 220-229, XP000349672 ISSN: 0925-9635 page 220, left-hand column, line 11 - line 14 | 22 |
| A | TONG ET AL: "Layer splitting in hydrogen-implanted Si, Ge, SiC, and daimond substrates" APPLIED PHYSICS LETTERS, AMERICAN INSTITUTE OF PHYSICS. NEW YORK, US, vol. 70, no. 11, 17 March 1997 (1997-03-17), pages 1390-1392, XP002128656 ISSN: 0003-6951 abstract | 1-24 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern

Application No

PCT/IB 02/04723

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|---|---|---------------------|----------------------------|---------------------|
| US 5587210 | A | 24-12-1996 | US 5891575 A | 06-04-1999 |
| EP 0479625 | A | 08-04-1992 | AT 126355 T | 15-08-1995 |
| | | | AU 644218 B2 | 02-12-1993 |
| | | | AU 8559491 A | 09-04-1992 |
| | | | DE 69111960 D1 | 14-09-1995 |
| | | | DE 69111960 T2 | 08-02-1996 |
| | | | EP 0479625 A2 | 08-04-1992 |
| | | | JP 5150051 A | 18-06-1993 |
| | | | US 5216249 A | 01-06-1993 |
| | | | ZA 9107955 A | 24-06-1992 |
| EP 0282054 | A | 14-09-1988 | JP 1955860 C | 28-07-1995 |
| | | | JP 6058891 B | 03-08-1994 |
| | | | JP 63224225 A | 19-09-1988 |
| | | | JP 1940771 C | 09-06-1995 |
| | | | JP 6066273 B | 24-08-1994 |
| | | | JP 63224226 A | 19-09-1988 |
| | | | DE 3862326 D1 | 16-05-1991 |
| | | | EP 0282054 A1 | 14-09-1988 |
| | | | US 4863529 A | 05-09-1989 |

THIS PAGE BLANK (USPTO)